

DOE/JPL 954339-79/14
Distribution Category UC-63

FOURTEENTH QUARTERLY PROGRESS REPORT
Covering the Period January 1 to March 31, 1979

on

**EVALUATION OF SELECTED CHEMICAL PROCESSES
FOR PRODUCTION OF LOW-COST SILICON**
(Phase III)

JPL Contract 954339

Silicon Material Task
Low-Cost Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

by

J. M. Blocher, Jr. and M. F. Browning

May 30, 1979

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the U.S. Department of Energy, Division of Solar Energy.

The JPL Low-Cost Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

This report contains information prepared by Battelle's Columbus Laboratories under JPL subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology, or the National Aeronautics and Space Administration.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the capable assistance of the following individuals in the performance of the work and preparation of this report: Mr. James S. Fippin, Mrs. Pamela S. Kerbler, Mr. Erlan E. Rose, Mr. William A. Schmitt, Mr. David A. Seifert, Mr. William B. Thompson, Mr. Edgar A. Wasto, and Mr. Jack G. Wiley of Battelle's Columbus Laboratories; and Mr. W. R. Ackley and associates of Raphael Katzen Associates International, Inc., Cincinnati, Ohio.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS.	i
ABSTRACT.	1
INTRODUCTION.	3
EPSDU-RELATED ACTIVITIES.	4
PDU ACTIVITIES.	5
EXPERIMENTAL SUPPORT PROGRAM.	13
Wetted-Wall Condenser.	13
Fluidized-Bed Modelling.	14
Zinc Chloride Electrolysis	15
Zinc Vaporizer	17
PLANS FOR THE NEXT REPORT PERIOD.	20

FIGURE

Figure 1. Process Flow Sheet for PDU	6
--	---

TABLE

Table 1. Summary of ZnCl ₂ Product Electrolysis Experiments at 500 C	16
--	----

FOURTEENTH QUARTERLY PROGRESS REPORT
Covering the Period January 1 to March 31, 1979

on

EVALUATION OF SELECTED CHEMICAL PROCESSES
FOR PRODUCTION OF LOW-COST SILICON
(Phase III)

JPL Contract 954339

Silicon Material Task
Low-Cost Solar Array Project

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

from

BATTELLE
Columbus Laboratories

May 29, 1979

ABSTRACT

During this report period, a decision was made to defer the construction of the 50 MT Si/year Experimental Process System Development Unit (EPSDU) until FY 1980, and in the meantime to construct and evaluate, at full scale, four critical units of the EPSDU. The fluidized bed, zinc vaporizer, by-product condenser, and electrolytic cell have been combined with auxiliary units, capable of supporting 8-hour batchwise operation, to form the Process Development Unit (PDU), which is scheduled to be in operation by October 1, 1979. The design of the PDU and objectives of its operation are discussed in this report.

Pending completion of the PDU, work has continued in the area of experimental support. A wetted-wall condenser has been constructed in which zinc chloride, introduced in excess of that condensed, is used to wash down

the unreacted zinc and residual silicon accumulated as fine-particle solids. This condenser, fed with the by-product of the miniplant reactor ($\sim 1/10$ PDU rate), is scheduled for operation in early April to evaluate the wetted-wall condenser principle for this unique by-product mixture.

Improvements in the experimental electrolytic cell have led to power efficiencies around 40 percent, thus substantiating the pertinence of the Bureau of Mines experience with pure zinc chloride as a basis for what can be expected with the zinc chloride/zinc/silicon slurry of the present application.

As contrasted with earlier observations of segregation of larger particles in a fluidized-bed reactor with a flat-plate distributor, no segregation has been observed in the PDU/EPDSU model of the round-bottom-conic-section design. Such segregation would have been a convenient (but not necessary) basis for preventing the growth of such particles to the point of plugging the product withdrawal tube.

Data on the relative volatility of impurities from liquid zinc remain inconsistent and it has been decided to defer such experiments until the zinc vaporizer of the PDU is available for tests more representative of the PDU/EPDSU conditions.

INTRODUCTION

This Fourteenth Quarterly Report is the third of the Phase III effort at Battelle's Columbus Laboratories (BCL) for DOE/JPL on the Evaluation of Selected Processes for the Production of Low-Cost Silicon. Phase III has as its ultimate objective the construction and operation of a 50 MT Si/year Experimental Process System Development Unit (EPSDU) for the production of granular semiconductor-grade silicon by the zinc vapor reduction of silicon tetrachloride in a fluidized bed of seed particles.

During this report period, the decision was made to defer the construction of the EPSDU until FY 1980 and in the meantime to test the operation of several critical units of the EPSDU. These units are the fluidized-bed reactor, the reactor by-product condenser, the zinc vaporizer, and the electrolytic cell. The combination of these units and the auxiliary equipment to permit their operation is to be known as the Process Development Unit (PDU). The critical units of the PDU are to be of the full-scale EPSDU design so that their operability can be evaluated and appropriate changes made, if necessary, prior to committing them to operation in the EPSDU. It is believed that in this way, considerable time can be saved in the initial operation of the EPSDU that might normally be taken in design modification activities.

During the PDU program, it is planned that the compilation of bids on the EPSDU equipment and installation will be continued and updated in order that such information may be readily available when needed. At the same time, the experimental support program will be continued to provide information of value to the program that can be obtained in equipment of smaller size than that used in the EPSDU or PDU.

The various aspects of the program will be discussed in turn.

EPSDU-RELATED ACTIVITIES

During this report period, work was continued on assembling the cost quotations on the various items of equipment in the EPSDU design. In several cases, modifications of the design were made upon the advice of vendors to accommodate the fabrication process or the availability of materials.

Other modifications in equipment design and anticipated operating procedures, most of these minor, have been made as the result of several meetings of a review committee convened by BCL management to make sure that no significant factors have been overlooked in the design of the EPSDU. A major emphasis in that effort was on safety and environmental concerns.

The present status of this effort may be summarized as follows. Quotations have been received on all equipment, and bids for construction and installation have been obtained. The preliminary estimate based on this information indicated that the original estimate of \$1.6 million was not grossly in error; in fact, the construction/installation costs were bid at slightly less than that originally estimated. This effort has been deferred (1) in order to meet the PDU schedule and (2) to provide information which reflects costs later in CY 1979 -- the time of planned start-up of EPSDU effort. This is especially important in view of the current relatively high inflation rate. Plans are to contact vendors for revised cost estimates in July or August, 1979, with the intent of supplying JPL with a cost update for purchase and construction of the EPSDU by October 1, 1979.

PDU ACTIVITIES

As noted above, a combination of critical units from the EPSDU is to be constructed and operated in such a way as to validate the operability of these units or to obtain information leading to favorable modification of their design. This equipment, known as the Process Development Unit (PDU), includes a 7-inch-diameter fluidized bed of 25 MT/year capacity*, a reactor by-product condenser of the same capacity, and a 6,000-amp electrolytic cell for recovery of zinc and chlorine values from the by-product zinc chloride. The electrolytic cell is one of six in the EPSDU design, and hence will have to be operated for 24 hours to accommodate the zinc chloride produced in the 8 hours of fluidized-bed operation. A suitable holding tank will be provided to accommodate the by-product. Thus, it should be possible to operate the electrolytic cell and fluidized bed independently. The other critical unit of the EPSDU is the zinc vaporizer, unique in that hysteresis in the zinc vapor generation rate is avoided by direct inductive coupling to the zinc in a vaporizer of minimum thermal capacity.

Figure 1 is a schematic diagram of the PDU, showing the critical units mentioned above and the auxiliary equipment. Details of the design of the reactor, zinc vaporizer, and electrolytic cell with minor revisions to accommodate scheduling are shown in Figures 22, 23, and 25 of the Final Report on the Phase I and Phase II work.** The condenser design shown in Figure 24 of that same report has been revised significantly to simplify its construction, but the general size and principle of operation is unchanged.

The following modifications of the reported designs are planned for use in the PDU:

- (1) Reactor
 - (a) Graphite liner will be used instead of SiC or SiC-coated graphite, to accommodate a design

* One of the two 25 MT/year reactors in the 50 MT/year EPSDU.

** DOE/JPL 954339-78/11, July 9, 1978.

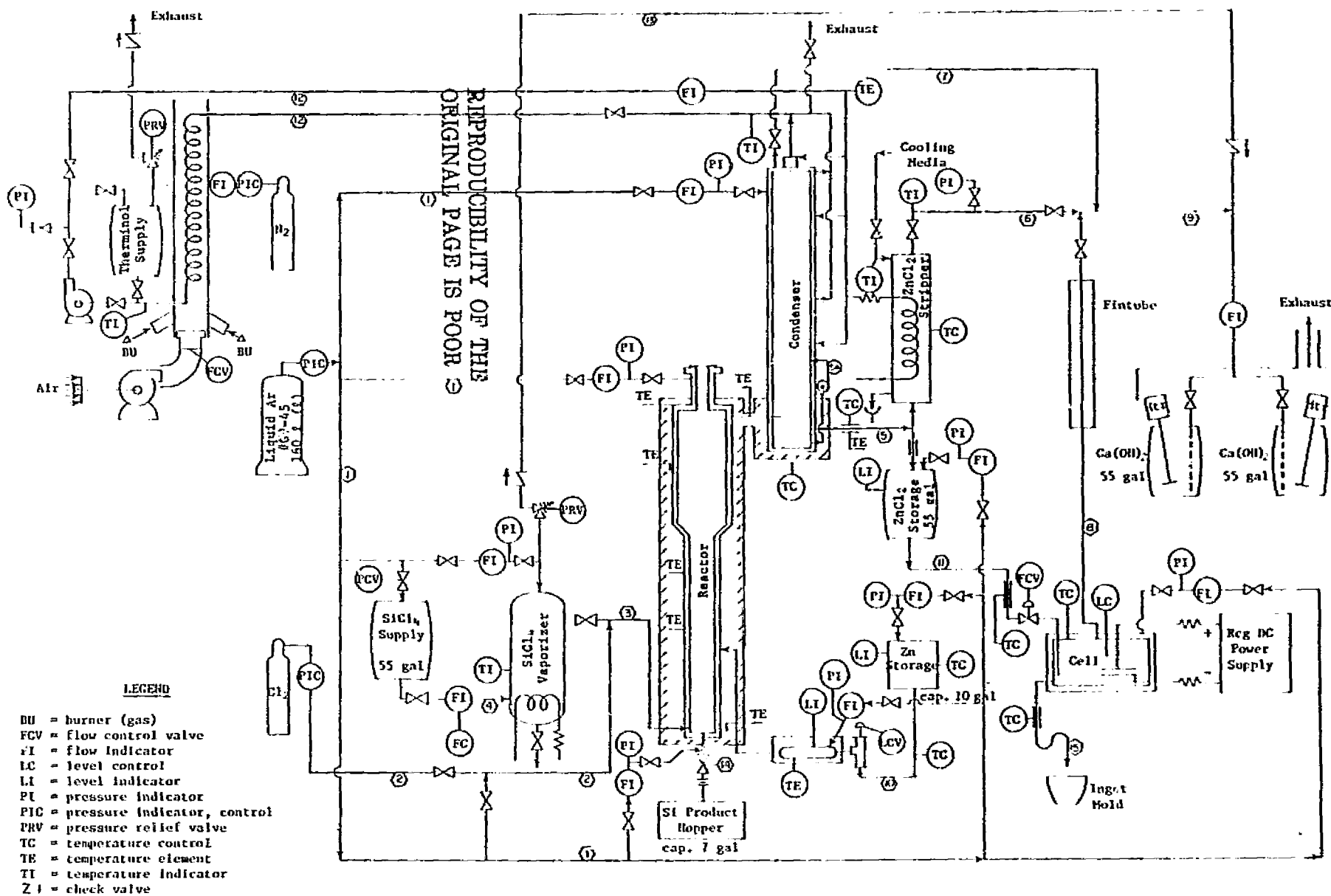


FIGURE 1. PROCESS FLOW SHEET FOR PDU

FIGURE 1 ADDENDUM

NOMINAL PROCESS STREAM COMPOSITION AND RATES

- | | | |
|----|--|---|
| ① | Argon, cumulative | |
| ② | $\text{Cl}_2(\text{g})$, 1.5 lb/hr (average of intermittent use*) | |
| ③ | $\text{SiCl}_4(\text{g})$, 80.0 lb/hr | |
| ④ | $\text{SiCl}_4(\text{l})$, 80.0 lb/hr | |
| ⑤ | $\text{ZnCl}_2(\text{l})$, (80.9-x) lb/hr** | $\text{Zn}(\text{s})$, 22.8 lb/hr |
| | $\text{ZnCl}_2(\text{s})$, x lb/hr | $\text{Si}(\text{s})$, 0.16 lb/hr |
| | $\text{SiCl}_4(\text{g})$, 29.6 lb/hr | $\text{Ar}(\text{g})$, 10.9 scfh |
| ⑤a | $\text{ZnCl}_2(\text{l})$, 2.4 gal/min | |
| ⑥ | $\text{SiCl}_4(\text{g})$, 29.6 lb/hr | |
| | $\text{Ar}(\text{g})$, 10.9 scfh | |
| ⑦ | $\text{SiCl}_4(\text{g})$, 1.4 lb/hr (average of intermittent use) | |
| | $\text{Cl}_2(\text{g})$, 0.3 lb/hr (average of intermittent use) | |
| ⑧ | $\text{Cl}_2(\text{g})$, 41.3 lb/hr (average of intermittent use) | |
| | $\text{SiCl}_4(\text{g})$, 1.0 lb/hr (average of intermittent use) | |
| ⑨ | $\text{SiCl}_4(\text{g})$, 32.0 lb/hr (average of intermittent use) | |
| | $\text{Cl}_2(\text{g})$, 41.6 lb/hr (average of intermittent use) | |
| | $\text{Ar}(\text{g})$, 10.9 scfh | |
| ⑩ | $\text{Zn}(\text{l})$, 61.6 lb/hr | |
| ⑪ | $\text{ZnCl}_2(\text{l})$, 80.9 lb/hr | |
| | $\text{Zn}(\text{s})$, 22.8 lb/hr | |
| | $\text{Si}(\text{s})$, 0.16 lb/hr | |
| ⑫ | ⑬ | Therminol coolant, rate to be determined |
| | ⑭ | Silicon product, 7.9 lb/hr + seed content |

* Averaged over time of operation of fluidized bed; actual rate = $K \times$ recorded rate, where

$$K = \frac{\text{operating time of fluidized bed}}{\text{operating time of chlorination or electrolysis}}$$

** x = small amount (e.g., <1 percent) of uncondensed ZnCl_2 .

- clarification, drawing approval, and purchase and construction schedule of 6 months
- (b) Seed hopper will be omitted, as no seed will be introduced during the 8-hour run period
- (2) Condenser, etc.
 - (a) Therminol coolant will be circulated in a tube on the outer shell and in an axially oriented well to improve operation and ease of construction
 - (b) A conventional grade of graphite (e.g., CS of UCC) will be used instead of a special impervious grade, to accommodate scheduling and to establish possible suitability
- (3) Zinc Vaporizer
 - (a) Outside diameter has been reduced to ~8 inches to get induction coupling required
 - (b) Insulation has been changed from Min-K to Kaowool for scheduling and economic considerations
- (4) Electrolytic Cell
 - (a) Electrode design has been modified to 11-degree sloping faces to improve power efficiency based on results of support studies.

The PDU provides for 8-hour operation requiring 640 pounds of SiCl_4 and 493 pounds of zinc, during which time about 60 pounds of silicon would be produced. As this represents about 0.6 cubic feet of bulk volume or 2.2 feet of bed height in the fluidized-bed reactor, product will be withdrawn during the run. However, as it will not be necessary to provide for seed replenishment during the run, that part of the EPSDU reactor design will not be reproduced.

Since the major objective of the PDU program is to verify the operability of the critical units with whatever design changes may be necessary, the need for high-purity reactants and the large amount of related purification,

present in the EPSDU design is obviated. Further, the amount of by-product created in the anticipated PDU campaign is not sufficiently large to justify the waste disposal equipment contemplated for the EPSDU.

Chlorine and chloride disposal will be handled simply by discharging these by-products into a calcium hydroxide slurry. On the basis of past experience with systems of this sort, it is estimated that one 55-gallon drum containing ~210 pounds of slurried Ca(OH)_2 would be required. The calcium hypochlorite plus hydrated silicon oxide slurry so generated will be allowed to settle. The liquid will then be flushed down the drain with excess water and the solid will be loaded into drums and disposed of as solid waste.

The zinc produced by the electrolysis of the zinc chloride will be cast into pigs for possible reuse or return for credit.

In all, the equipment of the PDU is reduced to the minimum required to support one four critical units, so that the emphasis can be placed on their operation.

Readers of this report who are familiar with the process will have no difficulty identifying the various pieces of equipment in Figure 1 and will readily appreciate their function. Thus, no detailed description of the PDU is undertaken here; however, it would be appropriate to point out that the chlorine supply (tank) depicted at the lower left of Figure 1 is for the purpose of chlorinating accumulations of silicon from the reactor wall when needed, either (1) to alleviate undue constriction or (2) to remove the silicon prior to reactor cool-down so as to avoid cracking of the reactor liner due to differential thermal expansion.

The Therminol system shown at the upper left of Figure 1 is used (1) to bring the condenser to operating temperature prior to making a run (heat supplied by burners to heat-exchange coil) and (2) to dissipate the heat of condensation during a run. With the reactor by-products cooled to 325°C^* to minimize carry-over of zinc chloride vapor, about 20 kw of heat will have to be dissipated from the condenser. Tank nitrogen is provided to pressurize and purge the Therminol system, while liquid argon provides the

* Melting point of $\text{ZnCl}_2 = 318^\circ\text{C}$.

source of purge and breathing gas for those sections of the PDU containing halides.

Present plans call for having the PDU constructed by September 30, 1979, and operating during the 4-month period October 1, 1979, through January 31, 1980, at which time it is planned that the construction phase of the EPSDU would be initiated.

It is anticipated that operation of the PDU will answer the following questions.

- (1) Will the $\text{SiCl}_4(\text{g})$ preheater (lower section of the fluidized-bed reactor) perform as designed? What is the available margin?
- (2) Can adequate control of the vaporization rate of zinc be exercised via induction heater power control? Can the zinc inventory in the vaporizer be monitored by its inductive characteristics? Can zinc vapor free of zinc mist be generated?*,**
- (3) Are the fluidization characteristics, shown to be satisfactory in the miniplant and in room-temperature modelling experiments, reproduced in the PDU reactor?
- (4) Can the proper gas purge and silicon granule flow balance be maintained in the product withdrawal tube so as to prevent condensation of zinc in the withdrawal tube?
- (5) Can the condensed by-product slurry containing an estimated 9 v/o of finely divided $\text{Zn}(\text{s})$ and $\text{Si}(\text{s})$ (0.2 v/o) be recirculated in the condenser so as to provide the wetted-wall action required for

* It is contemplated that these questions will be answered in separate experiments with the PDU zinc vaporizer before connecting it with the fluidized-bed reactor.

** It is essential that the amount of zinc mist entering the reactor be minimized, as it is known to lead to the formation of fine silicon needles.

operation of the condenser as designed?*

undesirable segregation of the finely divided Zn(s) and Si(s) be avoided before the 350 C slurry reaches the electrolytic cell at 500 C (above the melting point of zinc, 420 C)?

- (6) Can acceptable current and power efficiencies be maintained in the electrolytic cell despite the potential restriction of electrolyte flow resulting from increasing the anode area by 2.5 times that currently used at the Bureau of Mines, Reno Station? (Although the anode area is increased by 2.5 times, the length of the channel through which the electrolyte circulates is increased by a factor of only 1.4.)
- (7) Are the amounts of silicon wall deposit, gas-phase-nucleated silicon and entrained zinc chloride within the manageable limits predicted from miniplant experience?
- (8) Are the favorably high reaction efficiency (~60 percent) and silicon production rate (~30 lb/hr ft²) maintained in the larger reactor?
- (9) What rate of chlorination of the silicon wall deposit can be maintained at reasonable chlorine utilization efficiency? Does the time required for chlorination fit into a reasonable turn-around cycle?
- (10) Can the negative temperature gradient toward the top of the fluidized-bed reactor be maintained in the larger unit so that appreciably increased

* Preliminary information on this point should be forthcoming from wetted-wall condenser experiments being carried out in conjunction with the miniplant, but with slurry concentration ranging only up to ~2 v/o at the end of 10 runs (see page 13).

reaction efficiency can be gained as was observed in the miniplant?

- (11) Are there unforeseen problems with the critical equipment items or with other parts of the PDU whose early solution will benefit the EPSDU program?

EXPERIMENTAL SUPPORT PROGRAM

During the period covered by this report, a wetted-wall condenser experiment was readied in conjunction with the miniplant used in previous studies. In addition, experimental support work was continued in the areas of fluidized-bed modelling, zinc chloride electrolysis, and vaporization of zinc. These subjects will be discussed in turn.

Wetted-Wall Condenser

Although wetted-wall columns are used for condensation and absorption in industry, none is known to operate under the requirements of EPSDU, and the chances of finding useful information that is directly pertinent are regarded as slim. Accordingly, an experiment was devised in which the product of the miniplant (which should be representative of that expected from the EPSDU) is to be fed into a wetted-wall condenser, patterned in principle after that of the EPSDU/PDU design but of smaller size.

In the EPSDU reactor condenser, condensation occurs in three parallel 1.5-inch-diameter channels, each of 240-inch length. The by-product gases from the reactor enter the channels at 927 C at a linear flow rate of 8.2 fps. In the miniplant wetted-wall condenser, a single 1-inch-ID tube is provided with a 6-foot length.

In scaling the EPSDU condenser to the miniplant size, one must consider gas flow velocity in the tubes, Reynolds number, heat transfer area, and flow of ZnCl_2 per unit surface area, as well as total tube perimeter. Since it is obviously impractical to proportionally scale all of these factors, it was necessary to select those which were thought to contribute most to the condenser operation. After these factors were reviewed with RKAI, it was decided that the most practical approach to sizing which should provide useful information would be based on surface area. In addition, it would be best if the miniplant condenser was undersized so that its condensing capacity limit might more easily be determined. Accordingly, the area of the miniplant

condenser is only about 70 percent of that which would result from a direct size reduction based on plant production rates.

The nominal flow rate of liquid zinc chloride to the wetted wall of the miniplant condenser was chosen to be essentially that designed for the EPSDU condenser in terms of quantity per unit of condenser area, or 0.2 gallons per minute for the 1-inch-diameter tube. Provisions have been made to vary the zinc chloride flow rate, to obtain some idea as to the minimum quantity needed to maintain a wetted wall. With this information, the amount supplied in practice can be confidentially held in excess of the minimum, so as to prevent a dry wall condition and subsequent choking-off of the condenser tube.

At the end of the current report period, assembly of the equipment was 95 percent complete, and initiation of the experimental work early in April was anticipated. A fuller description of the equipment will be given when the experimental results are reported during the next quarter.

Fluidized-Bed Modelling

In the Thirteenth Quarterly Report (DOE/JPL 954339-79/13, February 15 1979), it was reported that although segregation of large particles had been observed near a flat-plate distributor in early work, no such segregation was observed in modelling experiments with the round-bottom/conic-section bed support design of the EPSDU (Figure 14, page 53 of Phase I/II Final Report, DOE/JPL 954339-78/11, July 9, 1978). It had been hoped that such segregation might be relied on to permit preferential discharge of the large particles to a degree that would preclude growth to the point of blocking the particle-withdrawal tube.

During this report period, the "large particle" size [amounting to about 0.1 w/o of the ~500- μ m (average) bed] was increased from 5000 μ m to 10,000 μ m. Again, no evidence of segregation was noted, the mixing action at the bed support plate being too intense in this design to permit the segregation observed with the flat plate.

As pointed out in the Thirteenth Quarterly Report, prohibitive growth of large particles is a problem only if part of the initial bed is left in the reactor for extended periods. For example, with a (constant) average particle size of 400 μm , a 1000- μm "large" particle will take 196 hours or 8 days to grow to 5000 μm at which time it may become of concern in terms of plugging the EPSDU product withdrawal tube (diameter = 0.79 cm or 7900 μm). Present plans call for withdrawing and screening the bed every week when the wall deposit is chlorinated. As long as that practice is followed, the growth of the "large" particles will not be a problem. However, if it is possible to extend the operating cycle beyond 1 week, "large" particle growth may become a controlling factor.

Zinc Chloride Electrolysis

In an effort to increase the power efficiency (decrease cell voltage) in the electrolysis of ZnCl_2 (~ 50 m/o in KJ1), work was continued in the experimental cell described in the Thirteenth Quarterly Report. The major variables investigated were the current density, slant of the electrodes, and electrode-to-wall clearance, the latter two factors being of potential importance in the release of chlorine gas from underneath the anode.

The data are given in Table 1, a continuation of Table 1, page 17 of the Thirteenth Quarterly Report.

Two runs (Nos. 18 and 20) were made at different times under baseline conditions:

4-degree-inclined planar 8.8-cm-diameter electrodes,
no grooves or holes, Salt Mix II, 1.27-cm electrode
spacing, 0.80 amps/ cm^2 current density, and 499-502 C
temperature.

The current efficiency values averaged 95.2 ± 1.5 amps/ cm^2 and the power efficiency, 36.3 ± 0.6 percent. Decreasing the electrode area by 25 percent* in Run No. 21 to increase the electrode-to-wall clearance had the effect of

* Two segments sliced off circular anode along parallel symmetrical chords ~ 3.2 cm apart.

TABLE 1. SUMMARY OF ZnCl_2 PRODUCT ELECTROLYSIS
EXPERIMENTS AT 500 C^(a)

Run Number(b)	Electrode Configuration	Electrode Spacing, cm	Current Density, amp/cm ²	Power Efficiency, percent	Current Efficiency, percent	Average Temperature, C
11	12-degree-inclined planar electrodes, Salt Mix I	1.27	0.79	35.6	96.5	502
12	12-degree-inclined planar electrodes, Salt Mix I, 25 percent reduced area, perforated anode(c)	1.27	0.79	38.7	96.2	503
17	12-degree-inclined planar electrodes, Salt Mix II, 25 percent reduced area, perforated anode(c)	1.27	0.80	42.5	99.5	499
18	4-degree planar baseline electrodes, no grooves or holes, Salt Mix II	1.27	0.80	36.9	96.7	502
19	12-degree-inclined planar electrodes, 25 percent reduced area, no grooves or holes, Salt Mix II	1.27	1.58	30.8	100.1	512
20	4-degree-inclined planar baseline electrodes, as No. 18, Salt Mix II	1.27	0.80	35.7	93.7	499
21	4-degree-inclined planar baseline electrodes, as No. 18, Salt Mix II 25 percent reduced area	1.27	0.79	37.9	93.6	499

(a) ZnCl_2 by-product of the miniplant. Salt Mix I contained ~98.9 percent ZnCl_2 , 0.1 percent Zn, and 1.0 percent Si (miniplant by-product had been heated above the melting point of zinc to settle out the suspended zinc), admixed 55 m/o with 45 m/o KCl. In Salt Mix II, the Zn and Si contents were ~7.8 and ~2.2 percent, respectively.

(b) Runs Nos. 8 and 9 and 13 through 15 are not included because of minor technical problems which made the data suspect.

(c) 2.4-mm holes spaced 13 mm apart in hexagonal array.

increasing the power efficiency slightly (to 37.9 percent) in the direction expected for an increase in the ease of chlorine evolution and electrolyte circulation.

The highest power efficiencies (38.7 and 42.5 percent) were obtained in Runs Nos. 12 and 17, respectively, in which the greatest opportunity was provided for chlorine release (12-degree slant, perforated anode, 25 percent reduced in area).

The results of Run No. 11 with 12-degree tilted planar (unperforated) electrodes were not above baseline. However, it is believed that uncontrolled variables (mix inhomogeneity?) masked the real effect of the increased tilt (12 degrees versus 4 degrees). The presence of such uncontrolled variables is indicated by the incidence of two current efficiencies unrealistically high in the neighborhood of 100 percent (Runs Nos. 17 and 19).

The decreased power efficiency in Run No. 19 to 30.8 percent (compare Run No. 17, 42.5 percent) can be attributed to doubling the current density.

On the basis of these results, the 12-degree slant (actually 11 degrees, i.e., maximum tolerable within the cell) has been adopted for the PDU design. Initially, an unperforated anode will be used; however, the anode can easily be perforated for experiments related to that variable in the PDU.

Zinc Vaporizer

As discussed in prior reports, the vaporization of zinc at the controlled high rate required for the EPSDU reactor feed cannot be carried out by conventional means, for example, by boiling under pressure, controlling flow by a throttle valve, and monitoring flow by pressure differential across a sonic orifice. The high boiling point of zinc (908 C at 15 psia, 1043 C at 50 psia) and the corrosive nature of zinc liquid and vapor make this approach unattractive. However, it has been determined that induction heating energy can be directly coupled to liquid zinc in a vaporizer of low thermal capacity, so that the rate of vaporization can be controlled by the energy input, and the hysteresis of the vaporizer with change of energy input can be minimized to the point of promising good control over the vaporization

rate. The EPSDU vaporizer design based on this principle was shown as Figure 23, page 92 of the Final Report.

Two aspects of the zinc vaporizer design have been the subject of expanded support work, the induction heating characteristics of the vaporizer and the quality of the vapor obtained. Earlier work (Tenth Quarterly Report, DOE/JPL 954339-78/10, April 30, 1978) has confirmed that a vaporizer of this design is capable of supplying the ~ 1 pound per minute required for one of the two 25 MT/year units of the 50 MT/year EPSDU. However, that experimental vaporizer was tested with a rather closely coupled coil (~ 4 -inch ID), and it became of interest to determine how far the coil could be backed off to allow space for insulation. It was determined that with a five-turn, 10.75-inch-diameter coil, a 10-kw Lepel generator (450 kHz) would not vaporize zinc at the required rate, the maximum rate achieved being < 0.5 pound per hour. However, when the diameter of the five-turn coil was reduced to 8 inches, leaving an insulation space of 2.5 inches, the required rate was obtained even with insulation having a thermal conductivity of ten times that of the insulation (Babcock and Wilcox Min-K) planned for use in the EPSDU. Whether the use of Min-K as insulation for the 10.75-inch coil would have made possible a realization of the required vaporization rate is uncertain, as no total power output measurements were available which might justify such a conclusion. However, it is believed that with the larger coil, the coupling would have been so inefficient as to be inadequate, and that the tighter coupling of the 8-inch coil will be required for the EPSDU vaporizer.

The second point of interest with regard to the zinc vaporizer is the degree of purification obtained in the one-plate distillation inherent in the vaporization. Fortunately, metals such as iron and titanium are relatively non-volatile so that even with activity coefficients over unity, the equilibrium amounts of these elements reaching the vapor would be very small. For example, the iron content of the vapor should be only 10^{-9} that in the liquid zinc.

During the current quarter, vaporization experiments were undertaken to demonstrate this purification, with precautions taken to sample the starting

material, distillate*, and residue* as liquids so as to avoid the effects of segregation on freezing. Further, a reportedly better technique** was used for analysis of the iron, lead, and cadmium concentrations. Despite these changes, the material balances were unsatisfactory so as to cast doubt on the analytical results.

It is believed to be prudent to wait until the vaporizer of EPSDU design is available for the PDU and to carry out vaporization experiments with that unit. Consideration will be given to refinement of the analytical technique previously used, with the possible alternative of going to a radioactive tracer technique, which presumably could be made considerably more sensitive and specific.

* About 50 percent of the starting material.

** A newly acquired inductively coupled plasma spectrograph was used in place of the atomic absorption analysis used earlier.

PLANS FOR THE NEXT REPORT PERIOD

The following tasks are planned for the months of April, May, and June.

- (1) Continue the PDU activity with the objective of having the unit ready for operation by October 1, 1979.
- (2) Initiate zinc vaporizer experiments as soon as the PDU zinc feed and vaporizer equipment have been assembled.
- (3) Continue the experiment support effort involving condenser design, zinc vaporization [Item (2) above], and other items as their need becomes apparent.
- (4) As time permits, assemble an updated cost estimate for the construction of the EPSDU.